Thermal stability and nitrogen redistribution in the ⟨Si⟩/Ti/W–N/Al metallization scheme

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Backscattering spectrometry, Auger electron spectroscopy, and x-ray diffraction have been used to monitor the thin-film reactions and nitrogen redistribution in the ⟨Si⟩/Ti/W–N/Al metallization system. It is found that nitrogen in the W–N layer redistributes into Ti after annealing at temperatures above 500 °C. As a consequence of this redistribution of nitrogen, a significant amount of interdiffusion between Al and the underlayers is observed after annealing at 550 °C. This result contrasts markedly with that for the ⟨Si⟩/W–N/Al system, where no interdiffusion can be detected after the same thermal treatment. We attribute this redistribution of nitrogen to the stronger affinity of Ti for nitrogen than W. If the Ti layer is replaced by a sputtered $TiSi_{2.3}$ film, no redistribution of nitrogen or reactions can be detected after annealing at 550 °C for 30 min.

I. INTRODUCTION

Diffusion barriers are commonly used in contact structures to semiconductor devices to minimize interdiffusion between adjoining layers during postmetallization heat treatments. Various interstitial alloys like nitrides[1,2] and borides[3] have been investigated as diffusion barriers for integrated circuits applications. In a recent work, it was demonstrated that interdiffusion between Al and Si can be suppressed by an interposed layer of W–N alloy film up to temperatures as high as 600 °C.[4] However, in a realistic contact structure, it is always desirable to include an additional conducting film between the barrier layer and the Si substrate to provide good ohmic contact at the metal–semiconductor interface, particularly when the contact resistivities of the barrier on Si are unacceptably high.[5] In the present work, we investigate the thermal stability of the ⟨Si⟩/Ti/W–N/Al structure. Titanium is commonly used in both metal oxide semiconductor (MOS) and bipolar integrated circuits (IC's) to ensure low contact resistivity and good adhesion.[6] Also, a Ti underlayer relieves problems caused by hillock formation in Al interconnects.[7] Therefore, for successful application of W–N alloys as diffusion barriers, it is of practical interest to examine their chemical stability in the presence of an adjacent Ti layer in the metallization scheme.

II. EXPERIMENTAL PROCEDURE

Commercially prepared and polished *n*-type ⟨111⟩ Si substrates of resistivity ~0.005–0.01 Ω cm (⟨Si⟩) were used. Prior to loading into a sputter deposition system, the Si wafers were first oxidized slightly in an oxygen plasma for 10 min and then rinsed in deionized water, followed by etching in a 10% HF solution for 5 min at room temperature. Si wafers covered with thermally grown SiO_2 were also used. After an identical treatment by an oxygen plasma, these oxidized Si wafers were blown dry by nitrogen and then loaded for deposition. The sputtering system used had a base pressure of $\sim 7\times10^{-7}$ Torr achieved by a diffusion pump equipped with a liquid-nitrogen chiller trap. Titanium layers of ~1000–1500 Å were sputter deposited in a 10 mTorr argon ambient from a magnetron target at a rate of ~1100 Å/min. A substrate bias of −50 V was applied during Ti deposition. A $W_{70}N_{30}$ alloy film was then deposited by reactive sputtering in an ambient of 85% argon and 15% nitrogen at a rate of ~500 Å/min. Details of the W–N alloy depositions can be found in Ref. 4. An Al layer of about 2000–3000 Å was then sputter deposited at a rate of ~100 Å/min. The three layers were deposited sequentially in one pumpdown. Three different sample configurations were prepared: ⟨Si⟩/$W_{70}N_{30}$/Al, ⟨Si⟩/Ti/$W_{70}N_{30}$/Al, and SiO_2/Ti/$W_{70}N_{30}$/Al. Also, ⟨Si⟩/Ti/$W_{70}N_{30}$ and SiO_2/Ti/$W_{70}N_{30}$ samples (i.e., no Al overlayers) were obtained for nitrogen profiling analysis as described later. In some cases, diffusion barriers of composition $W_{54}N_{46}$ were also prepared.

Another set of samples with titanium silicide contact layers in lieu of Ti were also prepared. The titanium silicide films were sputter deposited from a composite $TiSi_2$ target at a rate of ~400 Å/min.

All as-prepared samples were subsequently annealed at temperatures from 500–600 °C in a vacuum of better than 5×10^{-7} Torr. A 2 MeV $^4He^+$ backscattering spectrometry (BS) was used to determine compositional profiles and to monitor interdiffusion or reactions in the samples. X-ray Read camera diffraction spectra were used for phase identification. Auger electron spectroscopy (AES) was used mainly to obtain information on the depth profile of nitrogen.

The characteristics of W–N alloy films were reported previously.[8] As-prepared $W_{70}N_{30}$ films are amorphous and crystallize at ~620 °C. $W_{54}N_{46}$ is polycrystalline. The sputter-deposited titanium silicide has a nominal composition of $TiSi_{2.3}$ as revealed by BS.

III. RESULTS AND DISCUSSION

A. Thermal stability of ⟨Si⟩/W–N/Al vs ⟨Si⟩/Ti/W–N/Al

Figure 1 shows the BS spectra of a sample of ⟨Si⟩/900 Å $W_{70}N_{30}$/2250 Å Al before and after annealing at 550 °C for 30 min. Nothing visibly changes in the depth profile as a

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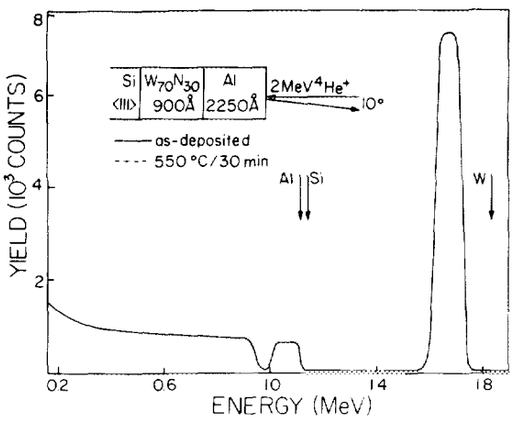

FIG. 1. A 2 MeV $^4He^+$ BS spectra of a sample of ⟨Si⟩/900 Å $W_{70}N_{30}$/2250 Å Al before and after annealing at 550 °C for 30 min.

result of annealing, in agreement with previous work.[4] This shows that the $W_{70}N_{30}$ layer effectively inhibits interdiffusion between Al and Si at 550 °C. On the contrary, significant interdiffusion is observed in the ⟨Si⟩/1500 Å Ti/940 Å $W_{70}N_{30}$/2400 Å Al sample after the same heat treatment (Fig. 2). Tungsten can be seen to outdiffuse to the surface leading to the formation of WAl_{12}, as revealed by x-ray analysis. A broadening of the leading edge of the Si signal is also observed and can be attributed to the onset of the formation of $TiSi_2$.[9] The metallurgical interaction that takes place in the ⟨Si⟩/Ti/$W_{70}N_{30}$/Al sample after annealing resembles that seen in the ⟨Si⟩/Ti/W/Al system subjected to the same thermal treatment.[10] Similar results are obtained when Si is replaced by SiO_2, which indicates that thermal instability of the ⟨Si⟩/Ti/$W_{70}N_{30}$/Al structure at 550 °C is not induced by the typically laterally nonuniform reaction of Ti with the substrate Si.[9]

The comparison of Figs. 1 and 2 demonstrates that the presence of a contact layer of Ti reduces the effectiveness of $W_{70}N_{30}$ alloy as a passive barrier between Al and Si. With a sublayer of Ti, $W_{70}N_{30}$ interacts with Al in a similar fashion

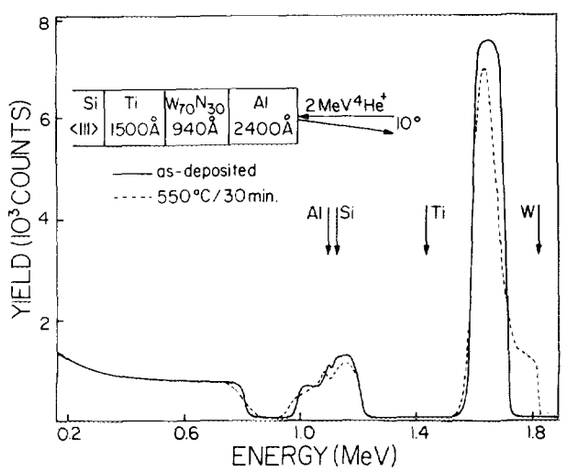

FIG. 2. A 2 MeV $^4He^+$ BS spectra of a ⟨Si⟩/1500 Å Ti/940 Å $W_{70}N_{30}$/2400 Å Al sample before and after annealing at 550 °C for 30 min.

as pure W does.[10] Similar results are obtained for systems with polycrystalline $W_{54}N_{46}$ barrier layers.

B. Bilayer of Ti/$W_{70}N_{30}$ on ⟨Si⟩ and on SiO_2

To further examine the cause of failure in the ⟨Si⟩/Ti/W–N/Al system, AES was used to determine the depth distribution of nitrogen before and after annealing. Figure 3 shows the changes in the AES depth profile of a sample of ⟨Si⟩/Ti/$W_{70}N_{30}$ as deposited [Fig. 3(a)], after annealing at 500 °C [Fig. 3(b)] and 550 °C [Fig. 3(c)] for 30 min. The nitrogen level in Ti can be observed to increase with annealing temperature, accompanied by a progressive drop of nitrogen in the $W_{70}N_{30}$ alloy layer. In other words, redistribution of nitrogen from W–N into Ti occurs. This movement of N deprives the $W_{70}N_{30}$ layer of nitrogen. The reaction of Ti and Si is also seen in the spectrum and is reflected in the step of the Si signal amplitude partway through the Ti layer. We have ascertained by AES that a bare W–N layer deposited on a ⟨Si⟩ substrate does not lose its nitrogen even after annealing at 700 °C; so the loss of nitrogen from the $W_{70}N_{30}$ film in the ⟨Si⟩/Ti/$W_{70}N_{30}$ sample after heat treatment is solely due to the presence of Ti. Although AES cannot provide accurate quantitative information of the nitrogen levels in the Ti layer (because of the overlapping of Ti and nitrogen Auger signals), AES does nevertheless give a convincing qualitative picture of the movement of nitrogen.

The BS spectra of a sample of SiO_2/1500 Å Ti/1200 Å

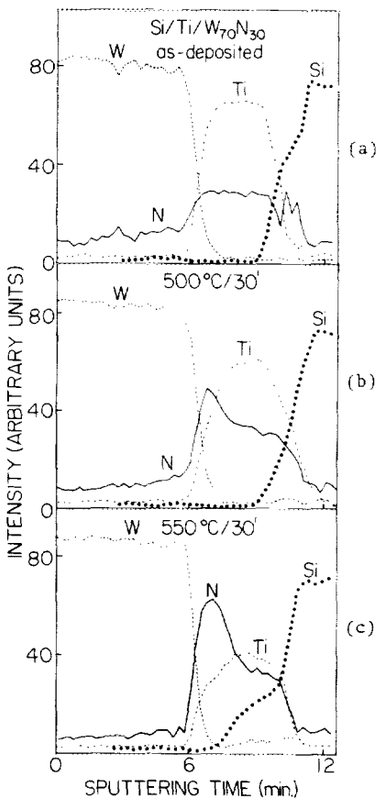

FIG. 3. AES depth profiles of a SiO_2/Ti/$W_{70}N_{30}$ sample: (a) as deposited; (b) after annealing at 500 °C for 30 min; and (c) after annealing at 550 °C for 30 min.

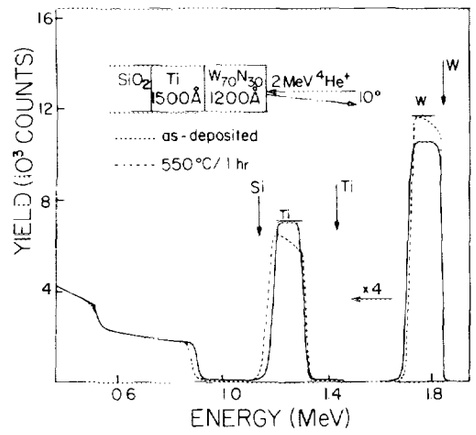

FIG. 4. A 2 MeV $^4He^+$ BS spectra of a SiO_2/1500 Å Ti/1200 Å $W_{70}N_{30}$ sample before and after annealing at 550 °C for 1 h.

$W_{70}N_{30}$ before and after annealing at 550 °C for 1 h are shown in Fig. 4. The expected signal heights for pure Ti and W are also shown. Since the nitrogen signal overlaps with the substrate signals, the amount of nitrogen in Ti or W was obtained from the height deficits of the observed Ti and W signals. It can be deduced that the amount of nitrogen (or oxygen) in Ti in the as-deposited samples cannot exceed 5 at. %. The signal height of Ti decreases, while that of W reaches almost the full height of pure W after annealing. This is consistent with the observation that nitrogen moves from the $W_{70}N_{30}$ layer into the Ti film, as shown by AES. Assuming that the W and Ti matrices do not contain any impurities other than nitrogen, one concludes that the Ti layer finally contains ~22 at. % of nitrogen after annealing, while the $W_{70}N_{30}$ film retains less than 10 at. % of nitrogen. The distribution of nitrogen in the W–N and Ti (or Ti–N) layers after annealing is probably nonuniform in depth, as a careful inspection of the BS spectra reveals. The percentages above represent average concentrations of nitrogen in Ti or W. In the x-ray spectra of the annealed SiO_2/Ti/$W_{70}N_{30}$ sample, W lines appear that are absent in the unannealed sample. These W lines were not observed for a sample of SiO_2/$W_{70}N_{30}$ (without Ti) taken through the same heat treatment. This proves that an adjacent layer of Ti is indeed responsible for the reduction of W–N into W. X-ray analysis, however, did not detect the formation of titanium nitride after annealing.

One obvious question to ask at this stage is what force drives the movement of nitrogen. If one compares the heat of formation of TiN ($\Delta H_{TiN} \sim -80$ kcal/mol) to that of W_2N ($\Delta H_{W_2N} \sim -17$ kcal/mol),[11] it follows that N is more strongly bound to Ti than to W by a large amount (63 kcal/mol or 2.7 eV/N atom). The redistribution of nitrogen from W–N into Ti is thus thermodynamically favorable. Also, the solid solubility of nitrogen in α-Ti is almost 10 at. % at 600 °C[12] (compared to < 1% for nitrogen in W at 600 °C[13]). As described above, the Ti layer contains, in average, ~22 at. % of nitrogen after annealing. This exceeds the solid solubility of nitrogen in Ti. A fraction of the nitrogen probably reacts with Ti to form nitrides or resides in the grain boundaries.

Crude estimations based on published diffusivities of nitrogen in W[13] and Ti[14] show that the diffusion length ($\sqrt{Dt}$) of nitrogen after an 550 °C, 30 min annealing is ~500 Å in Ti and 1000 Å in W. Our results show nitrogen is quite mobile in the Ti/$W_{70}N_{30}$ couple at temperatures above 500 °C.

It thus appears that the displacement of N into the Ti is driven by a chemical potential and facilitated by a high diffusivity. The resulting reduction of W–N to W then leads to an interaction between Al and W and the failure of the ⟨Si⟩/Ti/W–N/Al system.

C. Thermal stability of the ⟨Si⟩/$TiSi_{2.3}$/$W_{70}N_{30}$/Al system

One way to try to improve the stability of the Ti/$W_{70}N_{30}$ bilayer is to bind the Ti chemically to another element. A natural choice from the point of view of a contact is Si, to form $TiSi_2$. In this connection, it is noteworthy that the nitrogen depth profile of the ⟨Si⟩/Ti/$W_{70}N_{30}$ sample annealed at 550 °C [Fig. 3(c)] drops quite abruptly halfway through the Ti layer. BS analysis of a sample of ⟨Si⟩/Ti/$W_{70}N_{30}$ annealed at 600 °C for 30 min shows that a layer of $TiSi_2$ forms at the Si/Ti interface, with unreacted Ti remaining, probably containing nitrogen. As a comparison, analysis of Si/Ti/W taken through the same thermal treatment indicates that only a uniform $TiSi_2$ layer forms between Si and W with no unreacted Ti layer present. Nitrogen that moved into Ti from W–N evidently inhibits a complete silicide formation. A recent study of the formation of $TiSi_2$ from Si and nitrogen-implanted Ti by Ho[15] showed that nitrogen is "snow plowed" by the $TiSi_2$ reaction front leading to the segregation of nitrogen in an unreacted Ti layer. There also, the nitrogen concentration was observed to drop sharply at the Ti/$TiSi_2$ interface. Only a small amount of nitrogen was detected in the silicide layer. To further test the stability of the $TiSi_2$/$W_{70}N_{30}$ bilayer, we have analyzed by AES a SiO_2/$TiSi_{2.3}$/$W_{70}N_{30}$ sample after annealing at 550 °C for 1 h. A negligible change of the nitrogen distribution was noted.

A corresponding improvement of the stability of the whole metallization scheme ⟨Si⟩/Ti/$W_{70}N_{30}$/Al is thus expected if the Ti layer is replaced by $TiSi_2$. This was done by substituting a $TiSi_{2.3}$ film for the Ti. This ⟨Si⟩/$TiSi_{2.3}$/$W_{70}N_{30}$/Al sample was annealed at 550 °C for 30 min in a vacuum. No detectable interaction between Al and $W_{70}N_{30}$ or $TiSi_{2.3}$ is observed by BS. We thus conclude that for annealings up to 550 °C for 30 min, this contact scheme is metallurgically stable.

IV. CONCLUSION

We have shown that $W_{70}N_{30}$ alloys can be reduced to W in the presence of Ti upon annealing at 550 °C or above. This in turn is detrimental to the thermal stability of the ⟨Si⟩/Ti/$W_{70}N_{30}$/Al system. However, $W_{70}N_{30}$ is stable when a sputter-deposited $TiSi_{2.3}$ contact layer is used in place of Ti. This implies that a $TiSi_2$ layer formed by reacting Ti with Si prior to W–N and Al deposition should insure thermal stability of the contact structure up to 550 °C. Work is underway to examine various aspects of the redistribution

of nitrogen in greater detail. A good understanding of the compositional and microcrystalline characteristics as a function of sample processing is necessary for designing thermally stable contact structures with diffusion barriers.

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